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THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX

PART III

RELATIONSHIP OF VISCOSITY TO TEMPERATURE AND DRY-RUBBER-CONTENT

BY

H. Fairfield Smith

Summary

The relation of viscosity of latex or latex-water mixtures to temperature and d.r.c. can be described, to a first approximation, by an equation of the form

$$\log\eta = \log\eta_w + a + br$$

where η_w, the viscosity of water, indicates the change due to temperature; r = the ratio of rubber to serum (= d.r.c./(100 − d.r.c.)); and a and b are arbitrary constants.

Apparently the *relative* change of viscosity with temperature depends only on the suspension medium (serum), in accordance with the theory of viscosity of suspensions put forward by Einstein; and the viscosity of serum from 15 to 80°C is approximately proportional to that of water. A formula for $\log\eta_w$ as a cubic polynomial of temperature from 15 to 80°C has been evaluated (equation 3); but for practical use (*e.g.* in making temperature adjustments for observed viscosities) it will usually be more convenient to obtain the values of η_w from a published table.

Values of a and b for a series of concentrate-water mixtures, and of ammoniated field latices, are given in equations (4) and (5). Up to about 30 per cent d.r.c. the relative viscosity of latex seems to agree with the theoretical equation put forward by Guth *et al* (1937) for suspensions of spherical particles.

The purpose of this paper is to deduce from data given by Rhodes (1939 and unpublished) for viscosity of latices and of latex-water mixtures at varying temperature, mathematical formulae by which the observations may be succinctly described. These will serve as a convenient means for interpolation and for the deduction of quantitative estimates of the variation of latex viscosity with temperature and d.r.c.; and may facilitate comparison with the viscosity variation of other substances and with theories or hypotheses.

Data

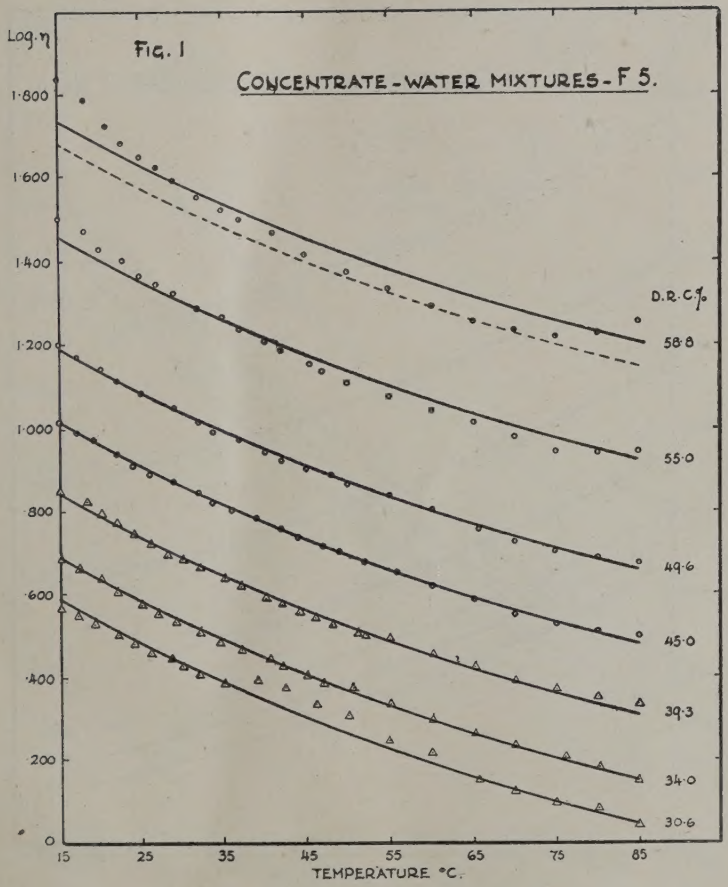
The data give viscosities at temperatures from 15 to 85°C for 14 samples of field latex of 32.5 to 39.3 per cent dry rubber content, preserved with liquid ammonia to an NH_3 content of 0.43 to 1.0 per cent; and for two centrifuged concentrates, and six mixtures of each with water, giving 14 suspensions varying from 30 to 59 per cent d.r.c. The NH_3 contents of the original concentrates were 0.9 and 0.43 per cent. For purposes of reference the field latices are numbered F_1 to F_3 and 1 to 11, and the two series of concentrates and concentrate-water mixtures are referred to as F_5 and F_6. The data for the F series have been published by Rhodes (1939) in whose paper the figures of corresponding number show graphs of viscosity in centipoises against temperature in degrees centigrade. The data for latices 1 to 11 have not previously been published.

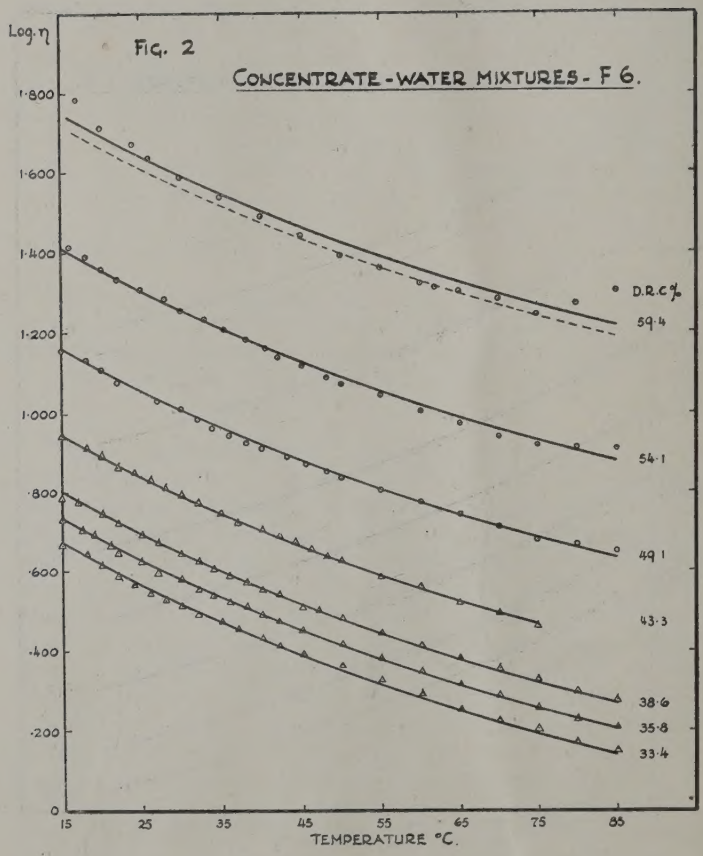
Viscosity determinations were made in a Höppler viscometer equipped with an "ultra-thermostat." Before being put into the viscometer all samples were clarified by centrifuging for 10 minutes at 2,000 revolutions per minute and decanting from the settled sludge.*

Each "observation" was recorded as the mean of two times of fall of either Ball no. 1 or no. 2 supplied with the viscometer. Since however successive observations of any one series through a range of temperatures appear to be correlated, the experiments cannot be considered to have been replicated in the usual statistical sense and valid experimental errors cannot be calculated. Differences between duplicate fall-times indicate that, for most of the data, the standard error of a single observation cannot be less than 0.4 per cent (in logarithms $\pm$ .002); miscellaneous evidence suggests that the total *random* errors may be not much greater. Concerning possible systematic (instrumental) errors we have little information. Comparison with data given by other workers suggests that observations at viscosities less than 20 cp. may be fairly reliable; but miscellaneous evidence suggests that observations greater than 30 cp. may be unreliable, and those between 20 and 30 cp. somewhat doubtful. This condition arises, presumably, because observations with the Höppler viscometer take no account of the rate of shear.

Computations in this paper are based on estimates of viscosities computed to 0.01 cp. Therefore they may not check exactly

* The latices and latex-serum mixtures, for which data were reported in part I (Communication 241), were clarified by passing through a 100-mesh sieve.


Log. η
Fig. 1
CONCENTRATE - WATER MIXTURES - F 5.
1·800
1·600
1·400
1·200
1·000
·800
·600
·400
·200
0
D.R.C.%
58·8
55·0
49·6
45·0
39·3
34·0
30·6
15
25
35
45
55
65
75
85
TEMPERATURE °C.


Log.η
FIG. 2
CONCENTRATE-WATER MIXTURES - F 6.
1·800
1·600
1·400
1·200
1·000
·800
·600
·400
·200
0
15
25
35
45
55
65
75
85
TEMPERATURE °C.
D.R.C%
59·4
54·1
49·1
43·3
38·6
35·8
33·4

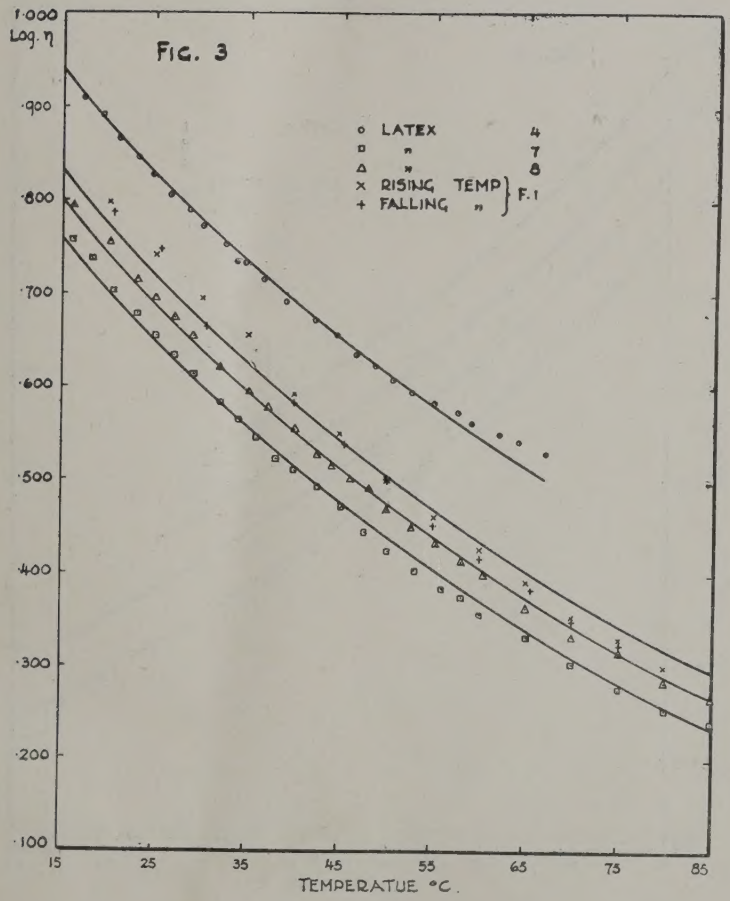


FIG. 3
Log. η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
·100
15
25
35
45
55
65
75
85
TEMPERATUE °C.
o LATEX 4
□ " 7
△ " 8
× RISING TEMP } F.1
+ FALLING " }

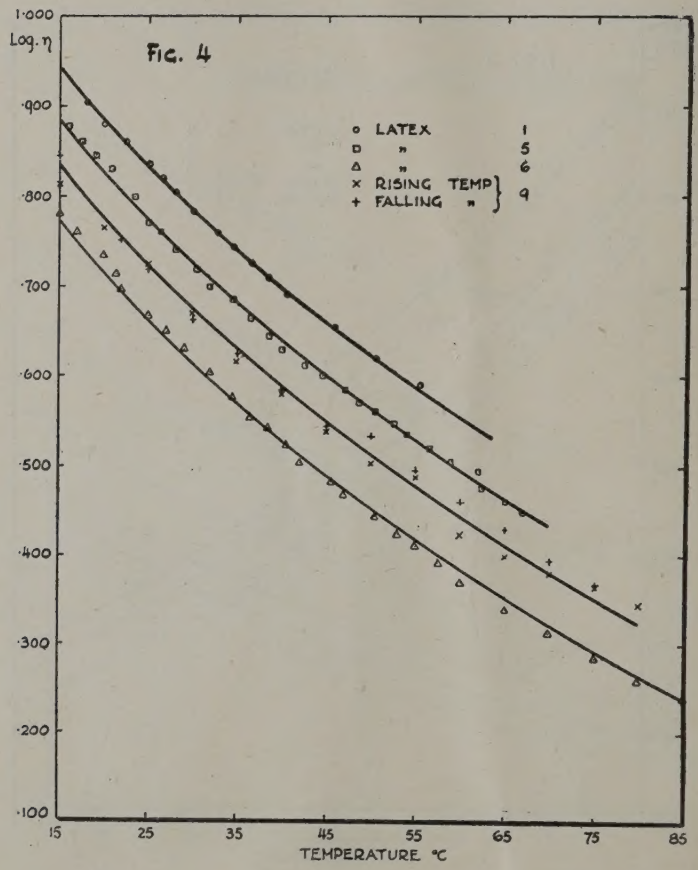


Fig. 4
Log. η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
·100
o LATEX 1
□ " 5
Δ " 6
× RISING TEMP } 9
+ FALLING " }
15
25
35
45
55
65
75
85
TEMPERATURE °C

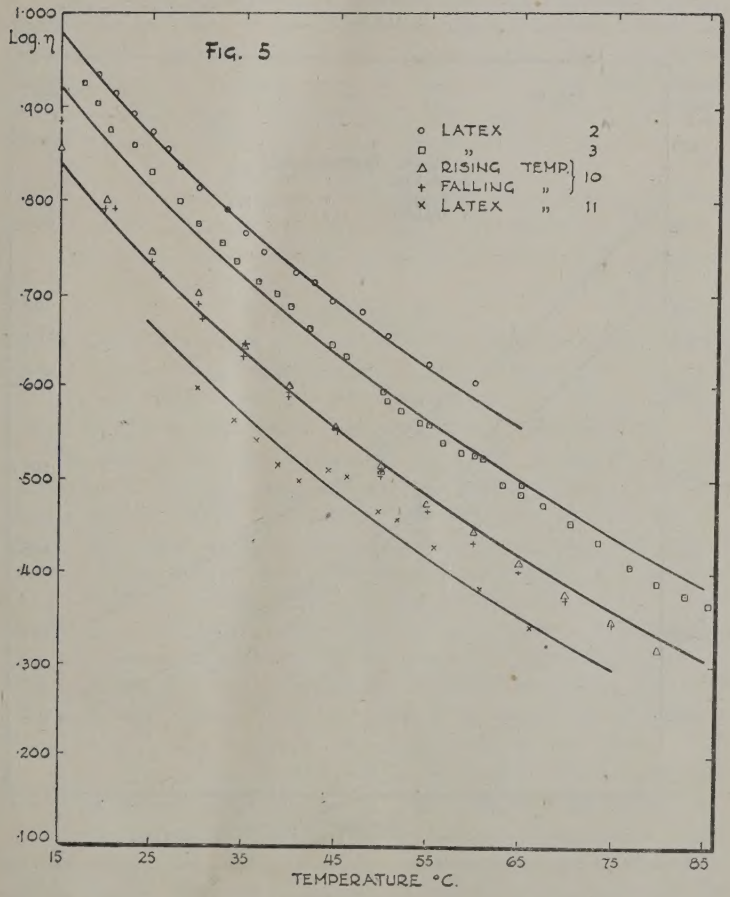


Fig. 5
Log. η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
·100
15
25
35
45
55
65
75
85
TEMPERATURE °C.
o LATEX 2
□ " 3
△ RISING TEMP. } 10
+ FALLING " }
× LATEX " 11

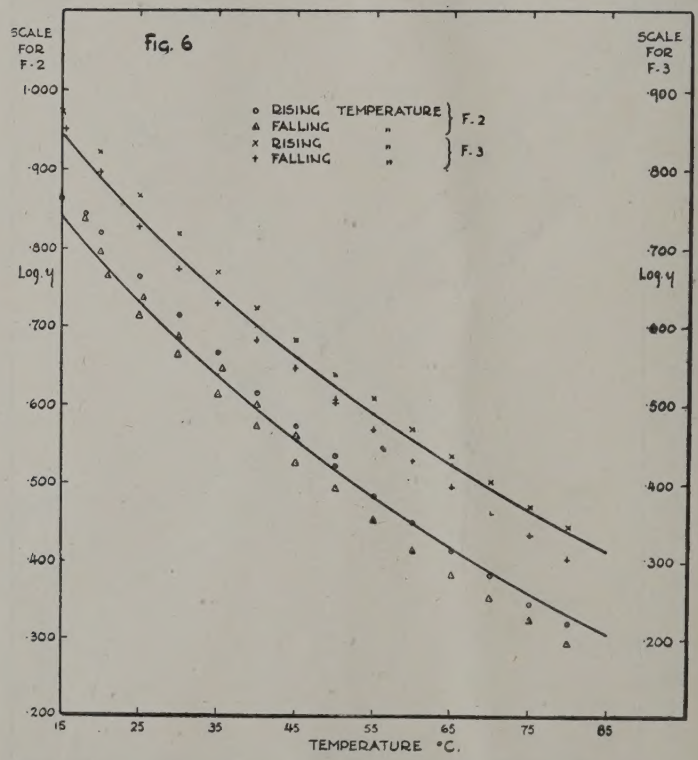


Fig. 6
SCALE FOR F·2
SCALE FOR F·3
o RISING TEMPERATURE } F·2
Δ FALLING "
× RISING " } F·3
+ FALLING "
Log. y
1·000
·900
·800
·700
·600
·500
·400
·300
·200
15
25
35
45
55
65
75
85
TEMPERATURE °C.

with computations repeated on the published figures which were given only to 0.1 cp.*

Variation of viscosity with temperature and d.r.c.

Figs. 1 to 6 show the logarithms of viscosities graphed against temperatures. The observed points indicate curves which are substantially parallel except for concentrates with viscosities greater than 20 cp. ($\log\eta$ greater than 1.3). The variation of viscosity with temperature and d.r.c. may therefore be described, to a first approximation, by an equation of the form

$$\log\eta = f_1(t) + f_2(\varphi) \qquad (1)$$

where $f_1(t)$ is some function of temperature, and $f_2(\varphi)$ is a function of d.r.c. and other latex characteristics such as serum solids.

The curves fitted to each series in figures 1 to 6 are given by

$$\log\eta = \log\eta_w + m \qquad (2)$$

where η_w is the viscosity of water, and m is a constant fitted for each latex (or concentrate-water mixture) and is equal to the average of $\log\ (\eta_s/\eta_w)$ where η_s is the observed viscosity of the suspension (latex or concentrate-water mixture) at each temperature.

For five of the field latices, *viz.* F_1, F_2, F_3, 3 and 10, the rate of change of viscosity with temperature seems to be greater than shown by the curve for water. The deviation is however not great, and until we have data observed at varying and known rates of shear, and for latices of known serum solids, it is scarcely worth while to examine these deviations in more detail. Since observations of $\log\eta_s$ greater than 1.3 are suspect, it is possible that the departure from the fitted curves of those relating to the 58.8 and 59.6 per cent concentrates is artificial; curves given by (2) with m estimated from (4) below, shown as dotted lines in Figs. 1 and 2, may be more correct than the observations.

Equation (1) may therefore be elaborated by expressing $\log\eta_w$ as a function of temperature, and m as a function of d.r.c.

No fundamental formula for the viscosity-temperature curve of water is known. For estimation in a given range a cubic polynomial seems to be as accurate as, and is more convenient for computation than, the numerous other formulae which have been suggested. The best fitting equation for $\log_{10}\eta_w$ as a third order polynomial of t in °C from 15 to 80°C, for viscosity in centipoises, is:

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* There are two misprints in table 1 of Communication 242, *viz.*
latex of fig. 6, 38.6% d.r.c., 55°C: for " 3.1 " read " 2.8 "
latex of fig. 6, 59.4% d.r.c., 80°C: for " 18.0 " read " 18.8 "

$$\log_{10}\eta_w = .2538 - .014394t + .00010198t^2 - .00000039604t^3 \quad \ldots \quad (3)$$
$$= -.0485 - .010037(t-25) + .000072278(t-25)^2 - .00000039604$$
$$(t-25)^3 \quad \ldots \quad (3a)$$

From 14 to 81°C this equation gives values of $\log\eta_w$ differing from the logarithms of the values in Critical Tables by less than .001 (estimates of η_w differing by less than 0.2 per cent).

Fig. 7 shows the values of m for the concentrate-water mixtures (F_5 and F_6) graphed against r_w = d.r.c./(100 − d.r.c.) = ratio rubber : serum by weight. Excluding, because of their suspected inaccuracy, the values for concentrates of d.r.c. greater than 58 per cent (r_w greater than 1.4), the regression of m on r_w is found to be

$$m = .0621 + 1.0905r_w$$
$$\pm .00755 \pm .00932 \quad (4)$$

For the ammoniated field latices (Fig. 8) the regression is

$$m = .062 + 1.3024r_w$$
$$\pm .0448 \quad \pm .0795 \quad (5)$$

The corresponding equation fitted to viscosities of 924 samples of field latex reported in Part I, Table I, but excluding samples with less than 28 per cent d.r.c. is (*cf.* equation 3 and Table IVa of Part I):

$$\log(\eta/\eta_w) = .253 + 1.0173r$$
$$\pm .00415 \quad (6)$$

and is shown as a broken line in Fig. 8. The difference between these and the latices reported above may be due in part to the different methods of clarifying the two series of latices, the older lot having been sieved, while the fourteen discussed above were centrifuged; it may also be due to source of latex, all the 14 samples having been obtained from the smallholding adjacent to the Institute.

Discussion

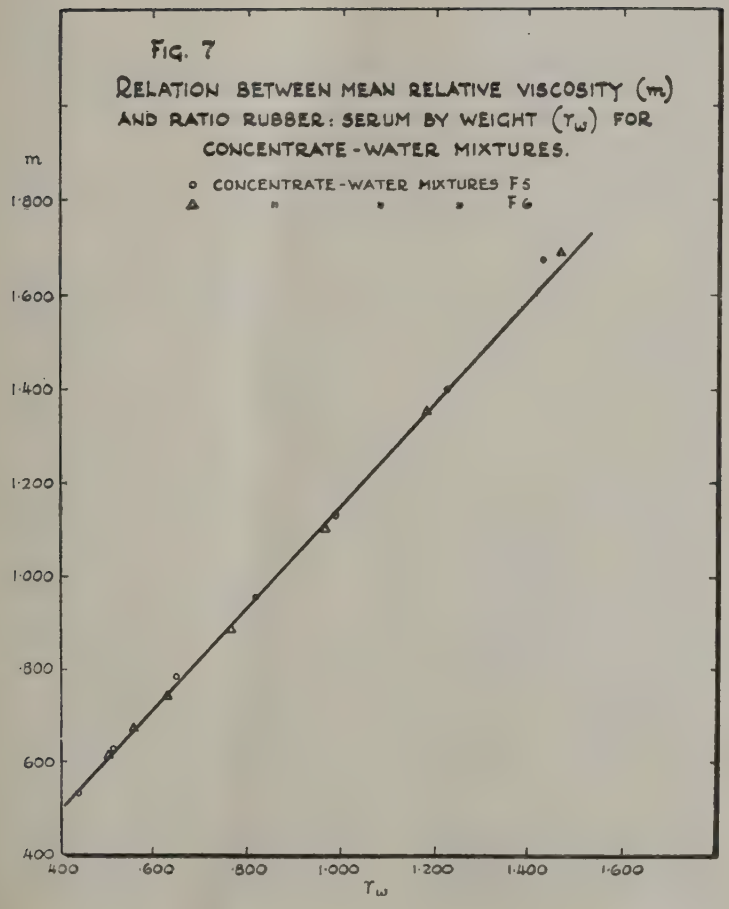
Viscosity: D.r.c.—In a previous communication (Rhodes and Smith, 1939) we fitted to data for the viscosities of latex-serum mixtures an equation of the form

$$\log(\eta + c) = \log(\eta_o + c) + br \quad (7)$$

But when there are no observations at very low d.r.c. the value of c in (7) cannot be satisfactorily evaluated and it is sufficient for empirical purposes in the region of 30 to 60 per cent d.r.c. to work with the linear equation

$$\log\eta = a + br \quad (8)$$

as has been done above (equations 4 and 5). Here a is an arbitrary constant greater than $\log\eta_o$.



Note on Figs. 7 and 8: *m* should be described as mean of *log* relative viscosity.

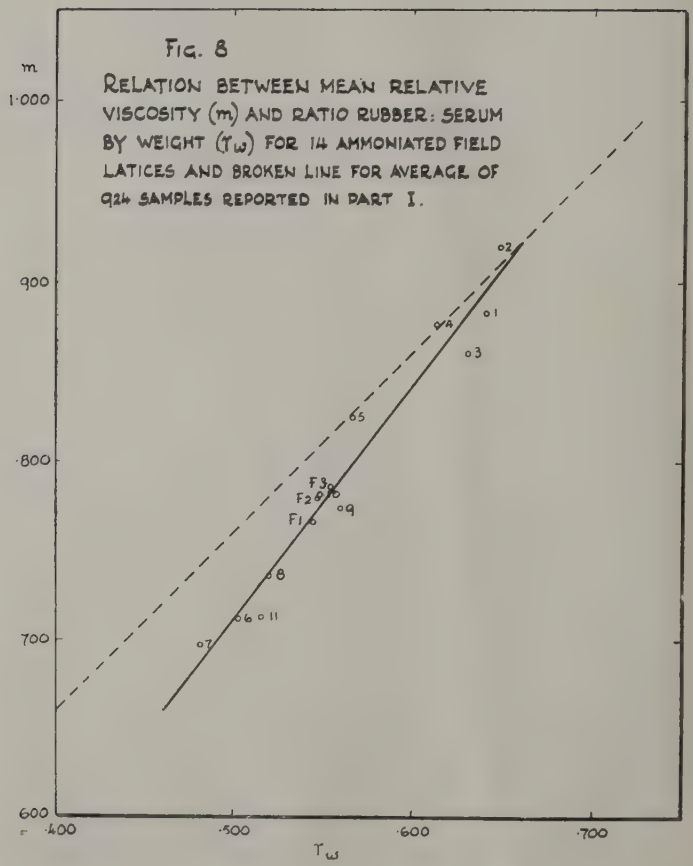


Fig. 8

Relation between mean relative viscosity (m) and ratio rubber: serum by weight (r_w) for 14 ammoniated field latices and broken line for average of 924 samples reported in part I.

In the previous paper we noted that the viscosity of diluted latex agreed fairly well with Guth's theoretical equation (derived from an elaboration of Einstein's theory) up to 15 per cent d.r.c. Unfortunately when writing that paper we overlooked that Guth's equation had been later modified by Guth, Gold and Simha to

$$\eta/\eta_o = 1 + 2.5\varphi + 14.1\varphi^2 \qquad (9)$$

where η_o is the viscosity of the suspension medium and φ is the volume concentration. This revised equation agrees fairly well with viscosity of diluted latex up to 30 per cent d.r.c.*

The data and formulae presented in this series of papers have been compared with available published data (Blow, 1929;† Bary, 1934; Bächle, 1936; Schmidt and Stamberger, 1937) as well as with Guth's equation. All show general agreement in principle although they exhibit considerable variation in detail. Owing to differences in material and methods (types of viscometers; method of expressing concentration *e.g.* weight or volume, total solids or dry rubber; using water or serum as the diluent and as control for determination of "relative" viscosities; variations in soluble and insoluble serum solids, affected by the period of storage of the latex, etc.,) a critical comparison is difficult and presentation of a review would seem to serve little useful purpose.

Viscosity: Temperature—Equation (2) implies that the viscosity of latex relative to viscosity of water is independent of temperature. Presumably this means that the viscosity-temperature curve of water shows viscosity proportional to that of the dispersion medium of latex; and equation (2) is in accordance with Einstein's theory in so far that it indicates that the viscosity of a suspension relative to the viscosity of its suspension medium may be a function of concentration independent of temperature.

For critical work attention should be paid to the solids content of serum, distinguishing between dissolved substances and suspended or colloidal particles. Since (by the Einstein-Guth theory)

* In comparing observations with Guth's equation on graphs representing log η against r it should be noted that the curve of Guth *et al* has a point of inflection at $r_v = .0888$, where $r_v = \varphi/(1 - \varphi)$. Therefore estimation of the slope of a curve such as (7) at zero concentration (as in Comm. 241, p. 179) is irrelevant for critical comparison with Einstein's theory. A further point to note in comparing latex viscosities with Einstein or Guth's theory is that φ represents the volume of total suspended matter, and if serum contains suspended or colloidal particles it is not strictly the suspension medium appropriate for comparison with that theory.

† Blow noted that latex-serum mixtures up to about 6 per cent d.r.c. agreed approximately with Einstein's theory.

A further paper which has only recently come to my attention is by Dogadkin, B.A. and Kovarskaya, B.M.—*Rubb. Chem. & Technol.* **11**: 630—643. Changes of viscosity there reported, both with temperature and with d.r.c., for dilutions of concentrated latex, revertex, etc., are much lower than those reported above.

all solid matter in suspension is expected to affect viscosity independently of its specific character and of temperature (except in so far as temperature may affect the volume concentration), the cause of variations in slope of the $\log\eta$: temperature curves of different latices should presumably be sought in the character and amount of soluble substances in the serum. For solutions of non-electrolytes η/η_w decreases with temperature, while for solutions of electrolytes it increases (Hatschek, p.114); therefore for an investigation of deviations of the curves for individual latices from equation (2), which are usually in the direction of η/η_w decreasing with temperature, one might take as an initial hypothesis that the differences of slope may be correlated with the amount of soluble non-electrolytes in serum.

It follows further from equation (2) that viscosity observations on latex or latex-water mixtures can be adjusted for temperature by the formula

$$\eta_v = \eta_u \frac{\eta_v'}{\eta_u'},$$

where η_u is the viscosity of latex at temperature u, etc.

η_u' is the viscosity of water at temperature u, etc.

u is the temperature of observation

v is the temperature at which estimation of viscosity is required. η_u' and η_v' can be obtained from tables (*e.g. Critical Tables*) or, if none such be available, can be calculated from equation (3).

This merely confirms the basis of the correction put forward by Jordan, Brass and Roe (1937); but the above formula is both more precise and more general, being applicable for any temperature range. Jordan *et al* noted that the temperature correction suggested by them was possibly an underestimate, but doubted the significance of a further digit estimated from their data. This paper indicates that their formula can be made more accurate as follows:

$$\eta_{25} = \eta_t \left\{ 1 + .023\ (t - 25) \right\}$$

For adjustments around 15°C the co-efficient is .026.

Acknowledgments

I am indebted to Dr. E. Rhodes and Mr. K. C. Sekar for the use of unpublished data observed in this laboratory by Che Abdul Wahid bin Abdul Wahab; and to Mr. W. S. Davey for criticisms during the writing of this paper.

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* I have been able to see only abstracts of this paper. Equation (9) was quoted by Eirich, F. and Goldschmid, O. (1938) *Kolloidzschr.* **81** 7—18; in the *Second Report on Viscosity and Plasticity,* p. 184. prepared by the committee for the study of viscosity of the Academy of Sciences at Amsterdam (1938); and in *Rubb. Chem. & Technol.* **11** 676.

Kuala Lumpur,

10th January, 1941.